Stereodefined Synthesis of a New Type of 1,3-Dienes by Ligand-Controlled Carbon−Carbon and Carbon−Heteroatom Bond Formation in Nickel-Catalyzed Reaction of Diaryldichalcogenides with Alkynes

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We have found that ligand control over the carbon−carbon and carbon−heteroatom bond formation on the nickel center provides an easy and convenient route to symmetrical (minor) and unsymmetrical (major) isomers of sulfur- and selenium-substituted 1,3-dienes. The unsymmetrical product is a new type of 1,4-substituted conjugated diene, which was readily synthesized from alkynes and diaryldichalcogenides. The unique feature of this developed one-pot transformation is total stereodefined synthesis of the diene skeleton, controlling not only the configuration of the double bond but also the *s-gauche* conformation of the central C−C bond. The mechanistic study revealed the key feature of alkyne insertion into the Ni−E and Ni−C bonds (E = S, Se), which governs the direction of the chemical transformation.

Introduction

Substituted conjugated dienes play an important role as building blocks in many fields of modern synthetic organic chemistry and material science. The most important applications include their use in the manufacture of pharmaceuticals, biologically active compounds, pheromones, and functionalized polymeric materials.[1–4] Symmetrical 1,4-heteroatom-substituted dienes R(E)C═CH−CH═C(E)R are accessible by various synthetic procedures;[4] unsymmetrical dienes of the type R(E)═CH−C(R)═C(E)H are not known (E = S, Se).

Over the last years we have developed stereo- and regioselective synthetic protocols to thio(seleno) alkenes via the atom-economic addition reactions of E−E and E−H bonds (E = S, Se) to the triple bond of alkynes.[5–7] The mechanism of E−E bond addition to alkynes involves oxidative addition, alkyne insertion, and C−E reductive elimination, leading to alkene **A** (path 1, Scheme 1).[8,5] It was shown that alkyne insertion into the second M−E bond followed by C−C reductive elimination led to a symmetrical diene of type **B** (path 2, Scheme 1).[9]

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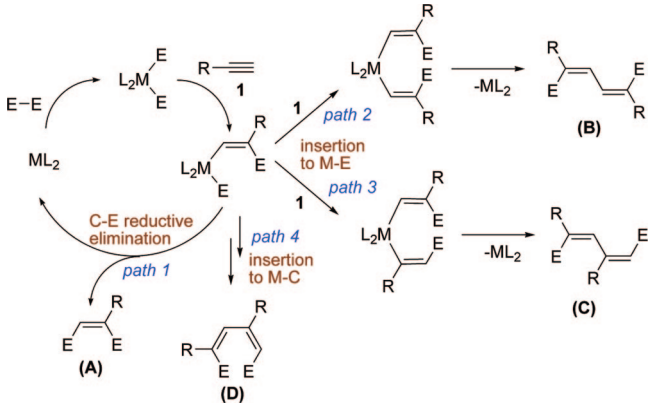
Scheme 1. Transition-Metal-Catalyzed Synthesis of Alkenes and Dienes



Alkyne insertion into the second M−E bond with reversed regioselectivity followed by C−C reductive elimination led to an unsymmetrical diene of type **C** as a side reaction (path 3, Scheme 1). In this case a mixture of **B** (major) and **C** (minor) products was obtained.[9,10]

Our idea was to suppress path 1, path 2, and path 3 and to change the direction of the second alkyne insertion into the M−C bond instead of the M−E bond followed by C−E reductive elimination, which would provide an easy and convenient synthetic approach to unsymmetrical dienes of type **D** (path 4, Scheme 1). To achieve this aim, at first we need to stabilize the transition metal intermediate $ML_2(CH{=}CER)(E)$ to a certain extent to allow insertion of the second alkyne molecule and to facilitate formation of a diene instead of an alkene. Second, very fine ligand control is required not only to suppress the formation of alkene but also to switch the direction of the insertion reaction to the M−C bond instead of the M−E bond.

In the present article we describe a novel approach to the selective synthesis of unknown thio- and seleno-substituted dienes (type **D**) in one step from readily available starting materials (terminal alkynes and organic disulfides or diselenides). Synthesis of the desired diene structure from these simple building blocks requires formation of not only carbon−heteroatom bonds but also a carbon−carbon bond under stereo- and regioselectivity controlled conditions, which is, obviously, a challenging problem. In addition to stereo- and regioselectivity control, assembling of diene **D** on a transition metal center revealed an unprecedented feature of the reaction, namely, preserving the *s-gauche* conformation of the diene skeleton. For several transformations involving dienes (Diels−Alder reaction, etc.[1–4]) the key role of the *s-gauche* conformation was reported;

Scheme 2. Ni-Catalyzed Ar_2E_2 Addition to Alkynes (E = S, Se)

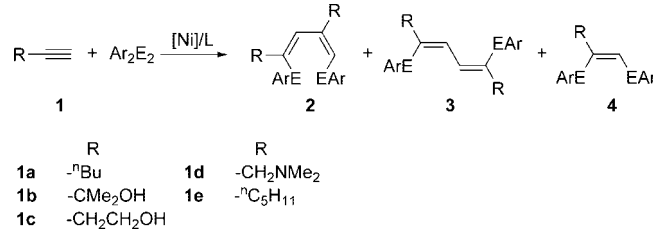


Table 1. Ni-Catalyzed Ph_2S_2 Addition to 1-Hexyne (1a)[a]

entry	ligand	conversion [%] of Ph_2S_2	**2a**:**3a**:**4a** ratio
1	PPh_3	96	32:15:53
2	$P(pMeOC_6H_4)_3$	96	43:19:38
3	DPPM	84	43:42:15
4	PPh_2Me	75	31:26:43
5	$PPhMe_2$	95	33:21:46
6	PPh_2Cy	80[b]	71:22:7
7	$PPhCy_2$	90[b]	74:26:0
8	PCy_3	85[b]	74:26:0

[a] Conditions: toluene, 70 °C, 3 h, 3 mol % $Ni(acac)_2$, and 30 mol % L. [b] Reaction time 1 h.

however, all known synthetic procedures available so far led to the more thermodynamically stable *s-trans* conformation.[11]

Results and Discussion

We have found that Ni complexes with phosphine ligands are able to facilitate the formation of the diene skeleton and the ratio of the products (**2**, **3**, and **4**) strongly depends on the nature of the ligand (Scheme 2).

Utilizing the PPh_3 ligand a mixture of dienes **2a** and **3a** and alkene **4a** was obtained, with the latter compound being dominant (entry 1, Table 1). The $P(pMeOC_6H_4)_3$ and especially DPPM ligands made it possible to decrease the contribution of the side reaction leading to alkene **4a** (entries 2, 3; Table 1). Encouraging results with DPPM inspired us to try other mixed PAr_xAlk_y phosphines. PPh_xMe_y ligands did not lead to any noticeable improvement (entries 4, 5; Table 1). However, excellent results were obtained with PPh_xCy_y ligands (entries 6−8, Table 1). The high activity of the catalyst made it possible to decrease the reaction time from 3 h to 1 h in the case of **1a** (entries 6−8, Table 1). Nearly complete conversion of Ph_2S_2 (90%) and the highest selectivity (76:24:0) were found in the case of the $PPhCy_2$ ligand, which totally suppressed the formation of alkene **4a**.

Further optimization of the reaction conditions showed that the reaction can be completed in 1 h in acetonitrile media with 96% conversion of the Ph_2S_2 and **2a**:**3a**:**4a** = 76:24:0 ratio of the products.[12] The catalytic reaction was found to be strongly dependent on the amount of the phosphine ligand in the system (Table 2). An excess of the ligand increased the reaction rate, but did not influence the selectivity. Among the studied range the fastest reaction was observed with 45 mol % of $PPhCy_2$ (entry 4, Table 2). Nevertheless, we have chosen 30 mol % for the synthetic procedure for economic reasons, taking into

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(10) We could assume an *s-trans* diene skeleton if this question was not addressed in the cited literature.

(11) The potential energy surface of rotation around the single carbon−carbon bond of the 1,3-diene is characterized by two minima with a C=C−C=C angle of 180° (*s-trans* conformation) and 38° (*s-gauche* conformation). The *s-cis* conformation with a C=C−C=C angle of 0° is a transition state; the second transition state is located at 102°. The *s-trans* conformation is thermodynamically the most stable. See:(a) Wiberg, K. B.; Rablen, P. R.; Marquez, M. *J. Am. Chem. Soc.* **1992**, *114*, 8654. (b) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *Organometallics* **2001**, *20*, 1652.

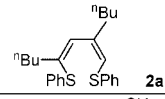
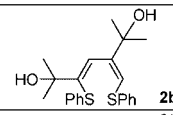
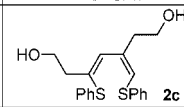
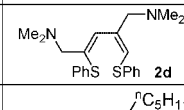
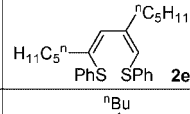
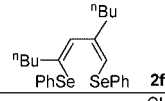
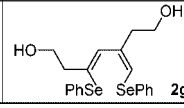
(12) See the Supporting Information for more details.

Table 2. Varying Ligand Amount in the Ni-Catalyzed Ph_2S_2 Addition to 1-Hexyne (1a)[a]

		conversion [%] of Ph_2S_2[b]	
entry	$PPhCy_2$, mol %	30 min	1 h
1	6	19	30
2	12	51	70
3	30	89	96
4	45	99	99

[a] Conditions: MeCN, 70 °C, 3 mol % $Ni(acac)_2$. [b] The ratio **2a**:**3a**:**4a** = 76:24:0.

Table 3. Scope of the Ni-Catalyzed Ar_2E_2 Addition to Alkynes

Entry	Alkyne	Ar_2E_2	Product	Yield, % [a]
1	**1a**	Ph_2S_2	 **2a**	70 [b]
2	**1b**	Ph_2S_2	 **2b**	75 [b]
3	**1c**	Ph_2S_2	 **2c**	71 [b]
4	**1d**	Ph_2S_2	 **2d**	62 [b]
5	**1e**	Ph_2S_2	 **2e**	67 [b]
6	**1a**	Ph_2Se_2	 **2f**	74 [c]
7	**1c**	Ph_2Se_2	 **2g**	69 [c]

[a] The isolated yield of **2** after purification. [b] Conditions: MeCN, 70 °C, 1−3 h, 3 mol % $Ni(acac)_2$, 30 mol % $PPhCy_2$, **1**:Ar_2E_2 = 3:1. [c] Conditions: MeCN, 40 °C, 5 h, 3 mol % $Ni(acac)_2$, 30 mol % $PPhCy_2$, **1**:Ar_2E_2 = 3:1.

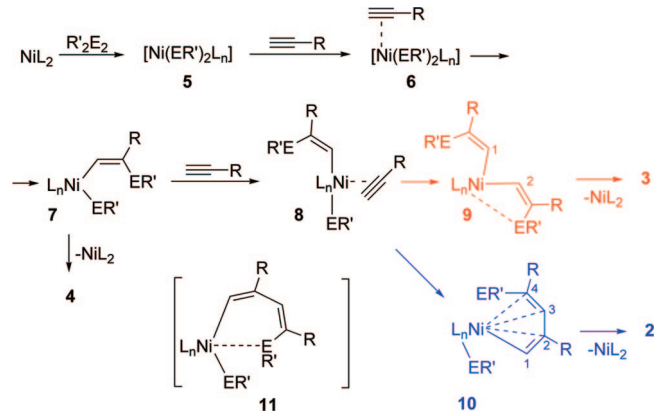
account that the catalytic reaction was completed within a reasonable time (entry 3, Table 2).

With an efficient protocol in hand for the synthesis of dienes **2**,[13] the scope of the reaction with different substrates was examined (Table 3). The developed catalytic system was tolerant to typical functional groups in alkynes (cf. entries 1−5, Table 3). Remarkably, the selenium-substituted dienes were also synthesized in the same manner via the reaction of Ph_2Se_2 and alkynes (entries 6, 7; Table 3). In all studied cases excellent selectivity was achieved resulting only in one type of double-bond configuration. The products were obtained in pure form after quick flash chromatography on silica with very good isolated yields of 62−75%. The side reaction leading to alkene **4** was totally suppressed and the yield of the symmetrical diene **3** was <26% in all studied cases.[12]

The mechanistic pathway of alkene **4** formation is well-known[5–7] and involves oxidative addition of the E−E bond to Ni(0), leading to **5**, followed by alkyne coordination to form the π-complex **6** and alkyne insertion into the metal−element

(13) See the Supporting Information for a detailed description of a reliable choice of solvent, temperature, etc.

Scheme 3. Plausible Mechanism of the Catalytic Reaction



bond[14] resulting in **7** (Scheme 3). C−E reductive elimination from complex **7** completes the catalytic cycle and releases the product **4**. By choosing an appropriate ligand we have stabilized intermediate **7** and its lifetime was enough to react with the second alkyne. To get some insight into the mechanism of this fascinating reaction, we have carried out theoretical calculations[15] of the alkyne insertion stage using a model system (Figure 1).

Theoretical calculations showed that starting from the π-complex **8** two pathways are accessible (Scheme 3). The first pathway involves alkyne insertion into the Ni−S bond and leads to bis(σ-vinyl) complex **9** with one of the vinyl groups coordinated to nickel in a chelate fashion due to interaction with the lone pair of the sulfur atom (Figure 1).

The calculated activation barrier was $\Delta E^{\ddagger} = 6.7$ kcal/mol, and the step was calculated to be exothermic by $\Delta E = -15.8$ kcal/mol. According to optimized bond lengths, both Ni−C1 and Ni−C2 were typical σ-bonds (Figure 1). The second pathway involves alkyne insertion into the Ni−C bond, and we expected formation of complex **11** (Scheme 3). Surprisingly, the calculations have shown that η^4-bonded dienyl derivative **10** was formed after the alkyne insertion step. According to optimized bond lengths, Ni−C1 was a σ-bond, while Ni−C2, Ni−C3, and Ni−C4 adopted π-bonding (Figure 1). The calculated activation barrier was $\Delta E^{\ddagger} = 4.6$ kcal/mol, and the step was highly exothermic by $\Delta E = -30.3$ kcal/mol.

The theoretical study revealed the unique feature of the Ni complexes to undergo insertion reactions involving both Ni−E and Ni−C bonds. According to the calculations, both insertion reactions are kinetically feasible, since the activation energies are rather small. However, complex **10** was found to be thermodynamically more stable by 14.5 kcal/mol compared to complex **9**, while **10-TS** is more stable than **9-TS** by 2.1 kcal/mol. Relative stabilities of transition metal complexes **9** and **10** and transition states **9-TS** and **10-TS** are the key factors responsible for preferable formation of diene **2** in the studied

(14) Several experimental studies have shown that insertion of terminal alkynes into the M−E bond (E = S, Se) is highly regioselective and leads to M−CH=C(R)E species, while the formation of M−CR=C(H)E species was not observed (see ref 5). Therefore, this pathway was not examined in our theoretical study.

(15) The calculations were carried out using the B3LYP density functional level with the Stuttgart/Dresden ECP basis set on the metal and the 6-311G(d) basis set on the other elements (see the Supporting Information for a complete description). In the previous studies it was established that this level of theory reasonably well describes the energy and geometry parameters of the systems involving transition metal complexes:(a) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **2002**, *124*, 2839. (b) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *Organometallics* **2005**, *24*, 715.

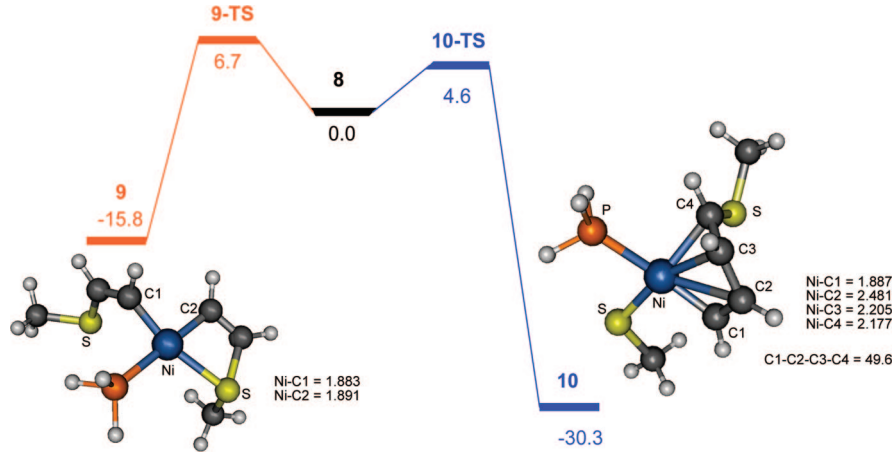


Figure 1. Calculated potential energy surface (in kcal/mol) at the B3LYP/SDD_6-311G(d) level for the model reaction (E = S, L = PH_3, R = H, R′ = Me) and optimized structures of **9** and **10** with selected bond lengths and dihedral angle (in Å and deg).

catalytic system. In total agreement with experimental findings, the calculations suggested that some minor amount of symmetrical diene **3** (from complex **9**) should also be formed.

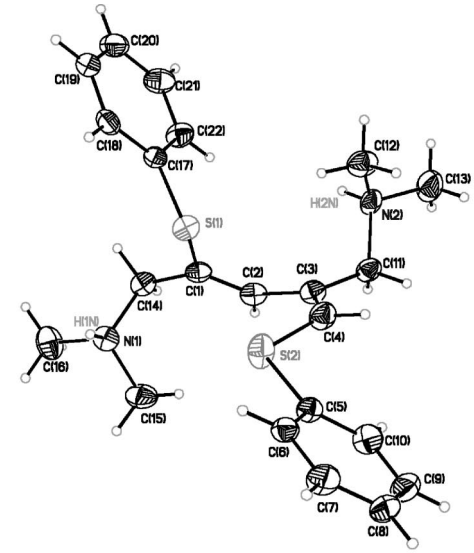
The influence of the amount of the ligand (Table 2) can now be easily rationalized taking into account that π-bonding in **10**, and donor−acceptor bonding in **9** should be broken to enforce reductive elimination and product release. This should increase the reaction rate, but does not affect the product ratio.

According to the dihedral angle C1−C2−C3−C4 = 49.6° in complex **10** (Figure 1), the diene skeleton was assembled in an *s-gauche* conformation, which was stabilized by η^4-binding to the metal. After dissociation of the diene from the metal center this conformation was preserved in solution and in the solid state. The *s-gauche* conformation of **2a** in solution was determined by NMR utilizing a 2D NOESY experiment. The molecular structure of diene **2d**, determined by X-ray analysis,[12] clearly confirmed the *s-gauche* conformation in the solid state, C1−C2−C3−C4 = 55.6° (Figure 2). The NMR spectra of **2a** and **2d** were not changed in a noticeable manner during a few days indicating that the s-*gauche* conformation is stable in solution at room temperature.[16]

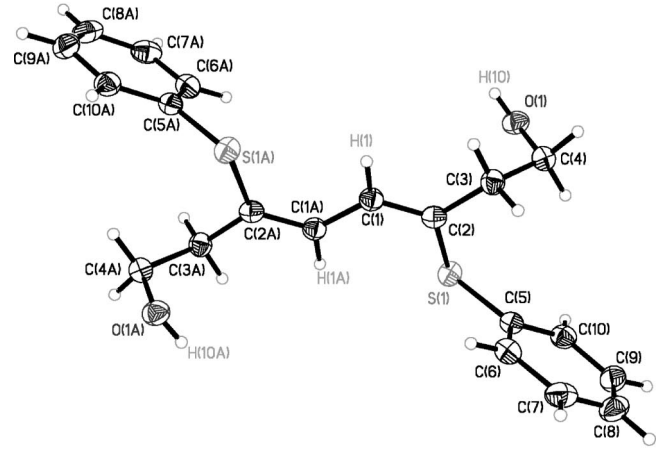
In complex **9** both vinyl ligands are bonded in a η^1-manner, which should result in a regular *s-trans* conformation of the diene skeleton. X-ray structure analysis of **3c** undoubtedly confirmed the *s-trans* structure with a dihedral angle of 180.0° (Figure 2).

In conclusion, we have developed a new efficient strategy for the synthesis of a new type of 1,4-chalcogen-substituted unsymmetrical 1,3-dienes. The overall procedure utilizes simple and readily available starting materials, and it is unique with respect to the high selectivity of the multistep diene formation. Optimal ligand selection for the Ni-catalyzed reaction led to a stereodefined synthetic procedure to control not only the configuration of the double bonds but also the conformation of the central single C−C bond. To the best of our knowledge, this type of dienes cannot be accessed by any other synthetic method with similar efficiency.

(16) There are two possible reasons for the observed stability of the *s-gauche* conformation: (1) thermodynamic reasons; for the synthesized dienes the *s-gauche* conformation is lower in energy than *s-trans*; and (2) kinetic reasons; the high energy barrier of rotation around the central C−C bond. The key difference between dienes **2** and **3** is the presence of substituent R in the 3-position of **2**, which should enhance the influence of both above-mentioned factors.



2d, C(1)-C(2)-C(3)-C(4) = 55.6°



3c, C(2)-C(1)-C(1A)-C(2A) = 180.0°

Figure 2. Molecular structures of **2d** (anionic part is omitted for simplicity[12]) and **3c** determined by X-ray analysis.

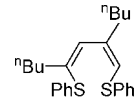
Experimental Section

General Synthetic Procedure for 2a−2g. Ph_2E_2 (5.0×10^{-4} mol), $PPhCy_2$ (1.5×10^{-4} mol, 41.2 mg), and $Ni(acac)_2$ ($1.5 \times$

10^{-5} mol, 3.9 mg) were dissolved in 0.2 mL of degassed MeCN, resulting in a dark brown solution. Alkyne (1.5×10^{-3} mol) was added to the solution, and the mixture was stirred at 70 °C (for E = S) or at 40 °C (for E = Se). Reaction time was determined by NMR monitoring (see Table 3 for the estimations of reaction time).

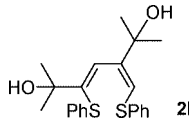
After completion of the reaction the products were purified by flash chromatography on silica with hexane/ethylacetate gradient elution (diene **2** was eluted after **3**). After drying under vacuum the pure products were obtained. The isolated yields given in Table 3 were calculated on the basis of the initial amount of Ph_2E_2 (E = S, Se).

Compound Characterization.



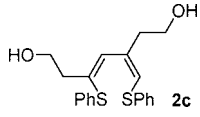
2a

[(*Z*,*Z*-2-Butyl-4-(phenylsulfanyl)-1,3-octadienyl)sulfanyl] benzene (2a): yellow oil, 70%. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; *J*, Hz): 0.83 (t, $J = 7.22$, 3H, CH_3); 0.90 (t, $J = 7.33$, 3H, CH_3); 1.23−1.31 (m, 2H, $-CH_2-$); 1.32−1.39 (m, 2H, $-CH_2-$); 1.44−1.54 (m, 4H, $-CH_2-$); 2.22 (t, $J = 7.10$, 2H, $-CH_2-$); 2.47 (t, $J = 7.45$, 2H, $-CH_2-$); 6.11 (s, 1H, HC═); 6.38 (s, 1H, HC═); 7.14−7.22 (m, 2H, Ph); 7.23−7.30 (m, 4H, Ph); 7.33−7.39 (m, 4H, Ph). ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm): 13.79; 13.92; 21.80; 22.38; 30.78; 30.86; 36.72; 36.99; 126.06; 126.31; 126.50; 128.84; 128.91; 129.65; 130.64; 131.00; 138.10; 140.53. Anal. Calcd for $C_{24}H_{30}S_2$: C 75.34; H 7.90; S 16.76. Found: C 75.44; H 7.97; S 16.42. Mass spectrum (EI): *m/e* 382 (M+, 5%).



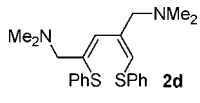
2b

***Z*,*E*-2,6-Dimethyl-3-(phenylsulfanyl)-5-[(phenylsulfanyl)methylene]-3-heptene-1,7-diol (2b):** light brown oil, 75%. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; *J*, Hz): 1.21 (s, 6H, $-CH_3$); 1.54 (s, 6H, $-CH_3$); 1.67 (br. s, 1H, OH); 2.80 (br. s, 1H, OH); 6.35 (s, 1H, CH═); 6.86 (s, 1H, CH═); 7.11−7.17 (m, 2H, Ph); 7.18−7.24 (m, 2H, Ph); 7.26−7.33 (m, 2H, Ph); 7.34−7.39 (m, 2H, Ph); 7.39−7.44 (m, 2H, Ph). ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm): 29.68; 29.99; 73.46; 75.22; 122.12; 126.53; 126.68; 128.81; 128.97; 129.21; 129.40; 130.45; 136.44; 136.88; 143.21; 147.66. Anal. Calcd for $C_{22}H_{26}O_2S_2$: C 68.35; H 6.78; S 16.59. Found: C 68.25; H 6.79; S 16.25. Mass spectrum (EI): *m/e* 386 (M^+, 1%).



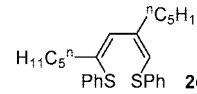
2c

***Z*,*Z*-3-(Phenylsulfanyl)-5-[(phenylsulfanyl)methylene]-3-heptene-1,7-diol (2c):** colorless oil, 71%. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; *J*, Hz): 2.42 (t, $J = 4.93$, 2H, $-CH_2-$); 2.51 (br. s, 1H, OH); 2.58 (br s, 1H, OH); 2.64 (t, $J = 4.74$, 2H, $-CH_2-$); 3.68 (t, $J = 4.93$, 2H, $-CH_2-$); 3.75 (t, $J = 4.74$, 2H, $-CH_2-$); 6.28 (s, 1H, CH═); 6.36 (s, 1H, CH═); 7.18−7.26 (m, 2H, Ph); 7.26−7.34 (m, 4H, Ph); 7.34−7.42 (m, 4H, Ph). ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm): 39.77; 40.04; 60.22; 60.88; 125.61; 126.55; 127.25; 128.94; 129.03; 129.17; 131.02; 131.49; 133.07; 135.44; 135.66; 135.71. Anal. Calcd for $C_{20}H_{22}O_2S_2$: C 67.00; H 6.19; S 17.89. Found: C 67.06; H 6.38; S 17.58. Mass spectrum (EI): *m/e* 358 (M^+, 2%).



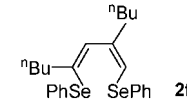
2d

***Z*,*E*-*N*,*N*,*N*′,*N*′-Tetramethyl-2-(phenylsulfanyl)-4-[(phenylsulfanyl)methylene]-3-pentene-1,5-diamine (2d):** light brown oil, 62%. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; *J*, Hz): 2.23 (s, 12H, $-CH_3$); 2.96 (s, 2H, $-CH_2-$); 3.25 (s, 2H, $-CH_2-$); 6.39 (s, 1H, CH═); 6.65 (s, 1H, CH═); 7.14−7.50 (m, 10H, Ph). ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm): 44.98; 45.20; 64.84; 65.08; 126.00; 126.42; 128.58; 128.87; 129.22; 130.93; 131.85; 134.73; 134.92; 135.78; 136.17. Anal. Calcd for $C_{22}H_{28}N_2S_2$: C 68.70; H 7.34; N 7.28; S 16.67. Found: C 68.40; H 7.40; N 7.15; S 16.30. Mass spectrum (EI): *m/e* 384 (M^+, 1%).



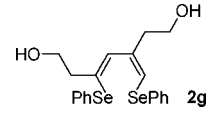
2e

[(*Z*,*Z*-2-Pentyl-4-(phenylsulfanyl)-1,3-nonadienyl)sulfanyl]benzene (2e): yellow oil, 67%. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; *J*, Hz): 0.84 (t, $J = 6.30$, 3H, $-CH_3$); 0.88 (t, $J = 6.87$, 3H, $-CH_3$); 1.21−1.25 (m, 4H, $-CH_2-$); 1.29−1.33 (m, 4H, $-CH_2-$); 1.47−1.55 (m, 4H, $-CH_2-$); 2.21 (t, $J = 7.33$, 2H, $-CH_2-$); 2.46 (t, $J = 7.45$, 2H, $-CH_2-$); 6.11 (s, 1H, HC═); 6.37 (s, 1H, HC═); 7.15−7.22 (m, 2H, Ph); 7.24−7.32 (m, 4H, Ph); 7.33−7.38 (m, 4H, Ph). ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm): 14.17; 14.21; 22.53; 22.67; 28.46; 28.51; 31.06; 31.68; 37.18; 37.40; 121.64; 126.22; 126.66; 128.89; 128.97; 129.03; 129.84; 130.15; 134.90; 137.22; 138.29; 140.81. Anal. Calcd for $C_{26}H_{34}S_2$: C 76.04; H 8.34; S 15.62. Found: C 76.18; H 8.57; S 15.42. Mass spectrum (EI), *m/e* 410 (M^+, 2%).



2f

[(*Z*,*Z*-2-Butyl-4-(phenylselanyl)-1,3-octadienyl)selanyl]benzene (2f): yellow oil, 74%. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; *J*, Hz): 0.83 (t, $J = 7.33$, 3H, $-CH_3$); 0.91 (t, $J = 7.45$, 3H, $-CH_3$); 1.26 (m, 2H, $-CH_2-$); 1.36 (m, 2H, $-CH_2-$); 1.49 (m, 4H, $-CH_2-$); 2.22 (t, $J = 7.33$, 2H, $-CH_2-$); 2.36 (t, $J = 7.45$, 2H, $-CH_2-$); 6.32 (s, 1H, CH═); 6.36 (s, 1H, CH═); 7.11−7.17 (m, 2H, Ph); 7.19−7.29 (m, 4H, Ph); 7.47−7.55 (m, 4H, Ph). ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm): 13.79; 13.90; 21.75; 22.40; 30.38; 31.23; 37.69; 38.16; 118.76; 126.71; 127.22; 128.88; 129.04; 129.74; 130.58; 131.82; 132.03; 134.05; 137.98; 142.58. ^{77}Se (95 MHz, $CDCl_3$; δ, ppm): 349.9; 378.3. Anal. Calcd for $C_{24}H_{30}Se_2$: C 60.50; H 6.35; Se 33.15. Found: C 60.71; H 6.22; Se 33.21. Mass spectrum (EI): *m/e* 478 (M^+, 1%).



2g

***Z*,*Z*-3-(Phenylselanyl)-5-[(phenylselanyl)methylene]-3-heptene-1,7-diol (2g):** colorless oil, 69%. ^{1}H NMR (500 MHz; $CDCl_3$; δ, ppm; *J*, Hz): 2.35−2.43 (br. s, 1H, OH); 2.42 (t, $J = 5.38$, 2H, $-CH_2-$); 2.52−2.57 (br. s, 1H, OH); 2.56 (t, J= 5.61, 2H, $-CH_2-$); 3.67 (t, $J = 5.38$, 2H, $-CH_2-$); 3.74 (t, $J = 5.61$, 2H, $-CH_2-$); 6.37 (s, 1H, CH═); 6.55 (s, 1H, CH═); 7.23 −7.30 (m, 6H, Ph); 7.48−7.54 (m, 4H, Ph). ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$; δ, ppm): 40.88; 40.97; 60.44; 60.55; 123.07; 127.12; 127.87; 128.36; 129.14; 129.21; 130.81; 131.91; 132.49; 134.29; 135.21; 138.91. ^{77}Se (95 MHz, $CDCl_3$; δ, ppm): 357.5; 371.3. Anal. Calcd for $C_{20}H_{22}O_2Se_2$: C 53.11; H 4.90; Se 34.91. Found: C 53.04; H 5.01; Se 34.88. Mass spectrum (EI): *m/e* 297 (M^+ − 157, 78%).

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Supporting Information Available: (1) General experimental procedure; (2) optimization of the reaction conditions; (3) yields and selectivity of the Ni-catalyzed reaction; (4) general synthetic procedure for **2a**−**2g**; (5) compound characterization; (6) description of the theoretical study; (7) description of the X-ray study; (8) Supporting Information for X-ray structures; (9) additional references. This material is available free of charge via the Internet at http://pubs.acs.org.

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